METHOD 9216

POTENTIOMETRIC DETERMINATION OF NITRITE
IN AQUEOUS SAMPLES WITH ION-SELECTIVE ELECTRODE

1.0   SCOPE AND APPLICATION

1.1   This method can be used for measuring nitrite in drinking water, wastewater, and reagent waters. If this method is used for other types of water samples (i.e., surface water, ground water, etc.), method precision and accuracy must be demonstrated for each matrix type.

1.2   The method detection limit is 0.05 mg/L of nitrite as nitrogen. Nitrite concentrations from 0.05 to 20 mg/L may be measured.

1.3   Ion selective electrodes (ISEs) must be used carefully and results must be interpreted cautiously. An ISE may be affected by numerous analytical interferences which may either increase or decrease the apparent analyte concentration, or which may damage the ISE. Effects of most interferences can be minimized or eliminated by adding appropriate chemical reagents to the sample. Obtaining the most accurate results, therefore, requires some knowledge of the sample composition.

NOTE: Manufacturers usually include a list of interferences in the instruction manual accompanying an ISE, along with recommended methods for minimizing or eliminating effects of these interferences.

2.0   SUMMARY OF METHOD

2.1   This method uses a nitrite-selective electrode. All standards and samples are mixed with an equal volume of nitrite interference suppressor solution (NISS). A calibration curve is constructed by recording the nitrite calibration standard readings using an appropriate meter or by manual plotting. Samples are then read in the same manner, and the concentrations reported by the meter or read from the graph.

3.0   DEFINITIONS

Refer to Chapter Three for the applicable definitions.

4.0   INTERFERENCES

4.1   Some anions, if present at high enough levels, are electrode interferences and will cause measurement errors. Table 1 displays the levels of possible interferences causing a 10% error. NISS is mixed in an equal volume with standards as well as with samples. For example, 25 mL of sample would be mixed with 25 mL of NISS. This procedure ensures that samples and standards are properly buffered, have a similar background and that no correction factor is needed for the dilution. Figure 1 shows how the nitrite electrode response changes with pH. This is compensated for by the addition of the NISS. Selectivity is mathematically demonstrated by the following equation:

$$E = E^{'} + s \log[c_j + \sum K_{ij} \, c_j^{Zj}]$$

Where: $E' = $ Reference potential

$s = $ Slope

$c_j = $ Primary ion concentration

$K_{ij} = $ Selectivity Coefficient

$c_j^{Zj} = $ Interfering ion concentration

$Zj = $ charge ratio of interfering ion

Successful analytical conditions depend upon:

$$c_j >> \sum K_{ij} \, c_j^{Zj}$$

4.2   Temperature changes affect electrode potentials. Therefore, standards and samples must be equilibrated at the same constant temperature ($\pm$ 1°C).

CAUTION: Use hood to avoid exposure to toxic gases released during acidification.

4.3   The user should be aware of the potential of interferences from colloidal substances and that, if necessary, the samples may be filtered.

4.4   Standard electrode filling solutions containing high levels of KCl should not be used as the reference electrode filling solution.

4.5   If electrodes are exposed to samples with nitrite concentrations greater than 20 mg/L, their response may become very sluggish when again measuring at a lower concentration. If this occurs, soak the electrodes for 8-12 hours in a mixture of the 0.5 mg/L standard and NISS.

5.0   SAFETY

5.1   Refer to Chapter Three for additional guidance on safety protocols.

5.2   It is the responsibility of the user to prepare, handle, and dispose of electrolyte solutions in accordance with all applicable federal, state, and local regulations.

6.0   EQUIPMENT AND SUPPLIES

6.1   A pH/mV meter capable of reading to 0.1 mV or an ISE meter.

6.2   Nitrite ISE (Orion 93-46 or equivalent) and double-junction reference electrode (Orion 90-01 or equivalent).

6.3   Thermally isolated magnetic stirrer, fluorocarbon (PFA or TFM)-coated magnetic stir bar, and stopwatch.

6.4   Volumetric flasks, 100 mL and 1 L - Class A.

6.5   Volumetric pipets, 5 mL, 10 mL and 50 mL - Class A

7.0   REAGENTS AND STANDARDS

7.1   Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2   Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

7.3   ISA adjustor solution (2M, $(NH_4)_2SO_4$): Dissolve 26.4 g of ammonium sulfate in reagent water to make 100 mL of solution.

7.4   Nitrite reference electrode filling solution (Orion 900046 or equivalent).

7.5   Nitrite interference suppressor solution (NISS) (Orion 934610 or equivalent).

7.6   1000 mg/L nitrite as N, stock standard - Weigh out 4.93 g of ACS reagent grade sodium nitrite that has been dried for 24 hours in a desiccator. Place in a clean one L volumetric flask. Add approximately 200 mL of reagent water and mix to dissolve. Add two drops of NaOH and make to volume. Mix by inverting 20 times.

7.7   100 mg/L nitrite as N, stock standard - Pipet 10.0 mL of the 1000 mg/L standard into a clean 100 mL volumetric flask. Make to volume and mix well. Replace this standard monthly.

7.8   10 mg/L nitrite as N, stock standard - Pipet 10.0 mL of the 100 mg/L standard into a clean 100 mL volumetric flask. Make to volume and mix well. Replace this standard weekly.

7.9   5 mg/L nitrite as N, stock standard - Pipet 50.0 mL of the 10 mg/L standard solution into a clean 100 mL volumetric flask. Make to volume with reagent water and mix well. This standard should be replaced daily.

7.10   1 mg/L nitrite as N, stock standard - Pipet 10.0 mL of the 10.0 mg/L standard into a clean 100 mL volumetric flask. Make to volume with reagent water and mix well. This standard should be replaced daily.

7.11   0.5 mg/L nitrite as N, stock standard - Pipet 5.00 mL of the 10.0 mg/L standard into a clean 100 mL volumetric flask. Make to volume with reagent water and mix well. This standard should be replaced daily.

8.0   SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1   All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

8.2   Samples should be stored at 4 $^{\circ}$C and must be analyzed within 48 hours of collection.

9.0 QUALITY CONTROL

9.1   Refer to Chapter One for specific quality control procedures.

9.2   Initial calibration verification standard (ICV): After performing the calibration step (Section 10.0), verify calibration by analyzing an ICV. The ICV contains a known nitrite concentration at the mid-range of the calibration standards and is from an independent source. ICV recovery must be 90-110 percent. If not, the source of error must be found and corrected. An acceptable ICV must be analyzed prior to sample analysis. The ICV also serves as a laboratory control sample.

9.3   Continuing calibration verification standard (CCV): After every 10 samples, and after the final sample, a CCV must be analyzed. The CCV contains a known nitrite concentration at mid-calibration range. CCV recovery must be 90-110 percent. If not, the error source must be found and corrected. If ISE calibration has changed, all samples analyzed since the last acceptable CCV must be re-analyzed.

9.4   Reagent blank: After the ICV and after every CCV, a reagent blank must be analyzed. A reagent blank is 25 mL of reagent water with 25 mL of NISS added. The indicated reagent blank concentration must be less than 1 mg/L nitrite. If not, the contamination source must be found and corrected. All samples analyzed since the last acceptable reagent blank must be re-analyzed.

9.5   Matrix spike: Follow the matrix spike protocols presented in Chapter One. The spike concentration must be 10 times the detection limit and the volume added must be negligible (less than or equal to one-thousandth the sample aliquot volume). Spike recovery must be 75-125 percent. If not, samples must be analyzed by the method of standard additions.

10.0 CALIBRATION AND STANDARDIZATION

10.1   When using a nitrate ISE and a separate double-junction reference electrode, ensure that reference electrode inner and outer chambers are filled with solutions recommended by the manufacturer. Equilibrate the electrodes for at least one hour in a 100 mg/L nitrite standard before use.

10.2   Calibrate the nitrite ISE using standards that narrowly bracket the expected sample concentration. If the sample concentration is unknown, calibrate with 0.5 mg/L, 1.0 mg/L, and 5.0 mg/L nitrite standards. Add 25.0 mL of a standard solution and 25 mL of the NISS into a 100 mL beaker to make each calibration standard.

10.3   Add a fluorocarbon (PFA or TFM)-coated magnetic stir bar, place the beaker on a magnetic stir plate, and stir at slow speed (no visible vortex). Immerse the electrode tips to just above the rotating stir bar. If using an ISE meter, calibrate the meter in terms of nitrite concentration following the manufacturer's instructions. If using a pH/mV meter, record the meter reading (mV) as soon as the reading is stable, but in no case should the time exceed five minutes after immersing the electrode tips.

10.4   Prepare a calibration curve by plotting measured potential (mV) as a function of the logarithm of nitrite concentration. For corrective action, consult the ISE operating manual.

11.0 PROCEDURE

11.1   Allow samples and standards to equilibrate to room temperature.

11.2   Prior to and between analyses, rinse the electrodes thoroughly with reagent water and gently shake off excess water. Low-level measurements are faster if the electrode tips are first immersed five minutes in reagent water.

11.3   Add 25.0 mL of sample and 25.0 mL of NISS to a 100-mL beaker. Add a fluorocarbon (PFA or TFM)-coated magnetic stir bar. Place the beaker on a magnetic stir plate and stir at a slow speed (no visible vortex). Immerse the electrode tips to just above the rotating stir bar. Record the meter reading (mV or concentration) as soon as the reading is stable, but in no case should the time exceed five minutes after immersing the electrode tips. If reading mV, determine nitrite-nitrogen concentration from the calibration curve.

11.4   When analyses have been completed, rinse the electrodes thoroughly and store them in a 100 mg/L nitrate standard solution. If the electrodes will not be used more than one day, drain the reference electrode internal filling solutions, rinse with reagent water, and store dry.

12.0 DATA ANALYSIS AND CALCULATIONS

Results must be reported in units commensurate with their intended use and all dilutions must be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1   Figure 2 displays a typical calibration curve for nitrite at 0.5 mg/L, 1 mg/L, and 5 mg/L. Figure 3 displays a low level calibration curve for nitrite at 0.05 mg/L, 0.1 mg/L, 0.2 mg/L, and 0.5 mg/L.

13.2   Table 1 displays the levels at which known interferences may impact the analysis. Refer to Sec. 4.0 for a discussion on interferences.

13.3   The following documents may provide additional guidance and insight on this method and technique:

13.3.1   "Determination of Nitrite in Foods and Wastewater Using a Nitrite-Selective Electrode", S.J.West, X.Wen, M.S.Frant, N.A.Chaniotakis, Pittsburgh Conference, March 1994.

13.3.2   "Determination of Nitrate, Nitrite, and Ammonia in Advanced Secondary Effluent by Means of Ion-Selective Electrodes", S.J.West, X.Wen, Pittsburgh Conference, March 1994.

13.3.3   Model 93-46 Nitrite Electrode Instruction Manual, ATI Orion, Boston MA, 1994.

14.0 POLLUTION PREVENTION

14.1   Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2   For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1.   Applications Laboratory Report, "Tests in Water Samples by Nitrite Electrode and 'Standard Methods' Colorimetric Analysis", ATI Orion, Boston MA, April 1995.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Table 1, Figures 1 through 3, and a flow diagram of the method procedures.

TABLE 1

NITRITE ELECTRODE SELECTIVITY DATA

Interfering Ion	log K_{ij}	10% Error Ratio (ppm)
Hydroxide	2.8	-
Fluoride	-3.1	170
Chloride	-3.1	320
Chlorate	-3.4	1600
Perchlorate	-3.1	830
Bromide	-3.0	570
Iodide	-1.2	15
Sulfate	-4.1	1100
Nitrate (N)	-3.3	200
Phosphate	-4.0	9500
Polyphosphate	-4.4	3400
Bicarbonate	-3.3	870
Acetate	-3.2	720
Lactate	-4.9	Very high
Phthalate	-2.5	380
Ascorbate	-4.2	Very high
Salicylate	-0.8	7.0

Source: Reference 1.

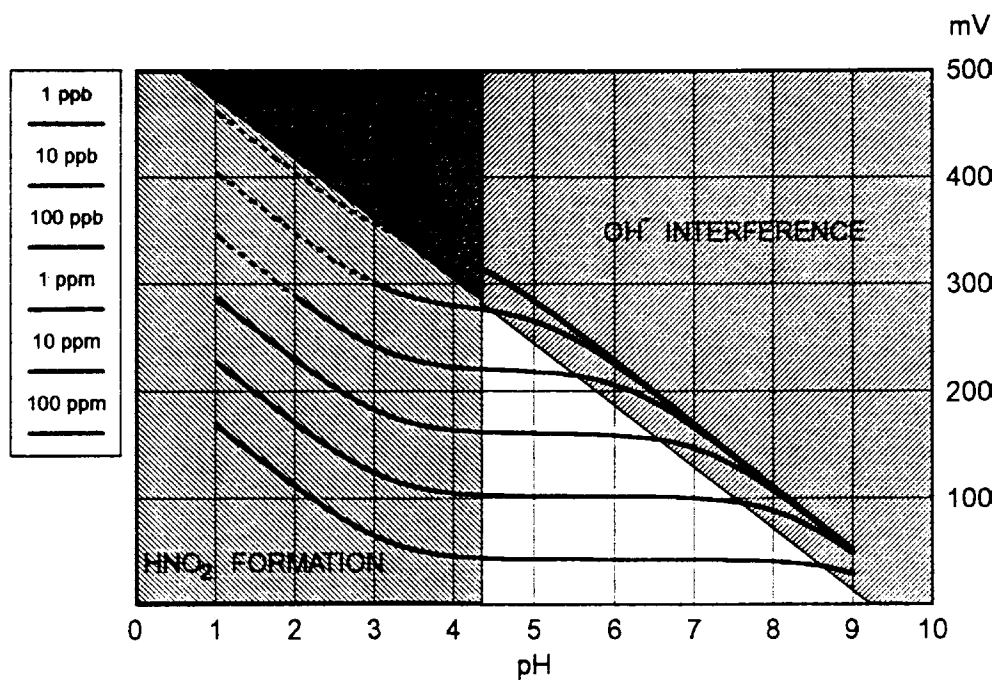# FIGURE 1

NITRITE ELECTRODE pH RESPONSE

FIGURE 2

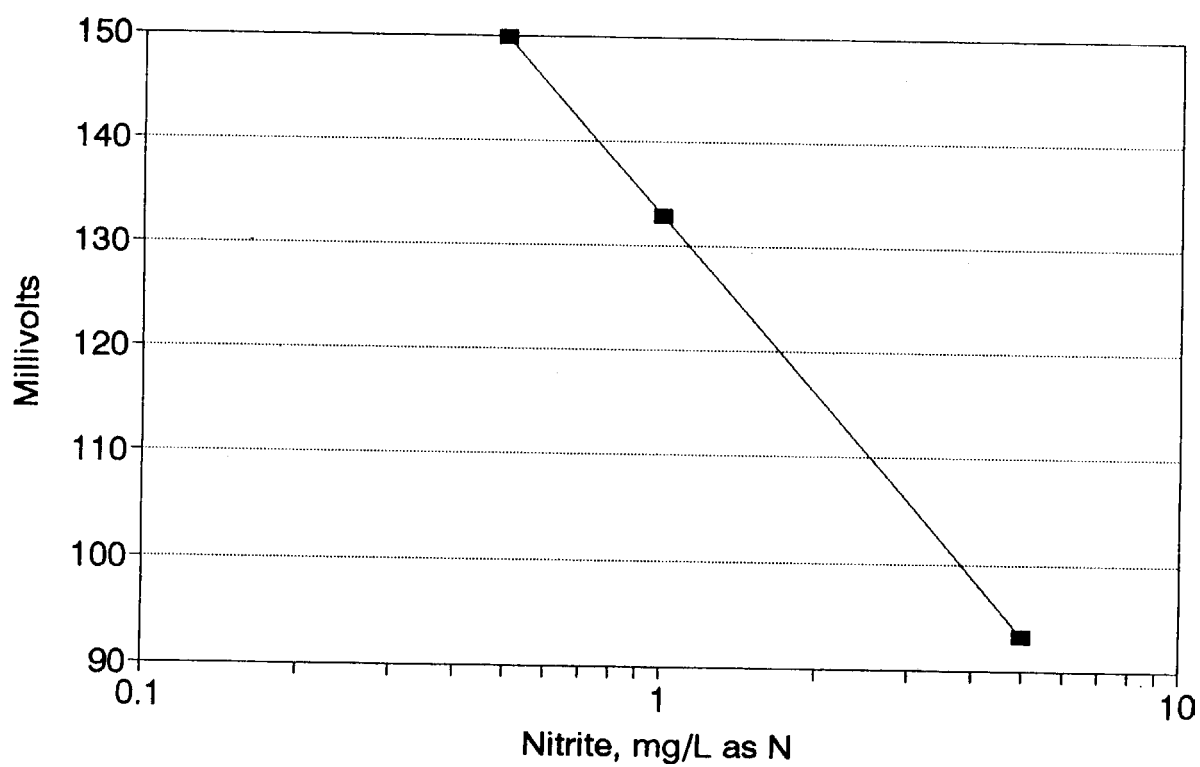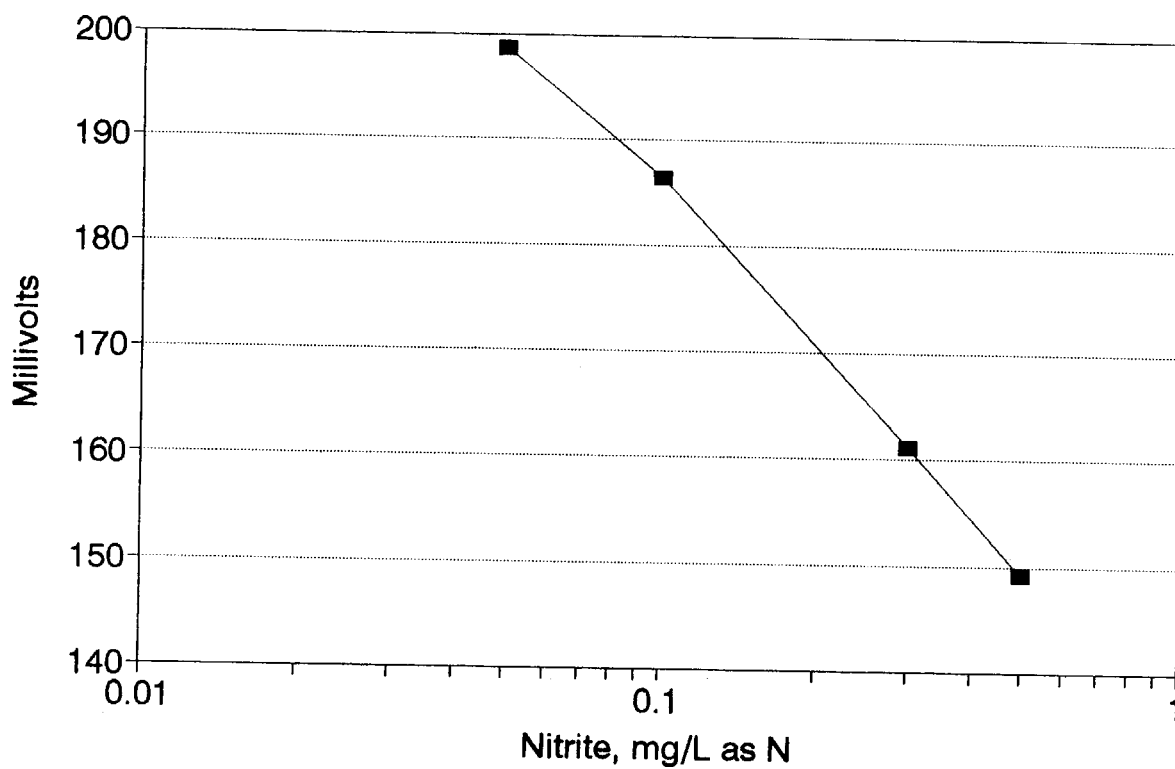## CALIBRATION CURVE FOR STANDARD LEVEL OF NITRITE

FIGURE 3

CALIBRATION CURVE FOR LOW LEVEL NITRITE METHOD

METHOD 9216

POTENTIOMETRIC DETERMINATION OF NITRITE
IN AQUEOUS SAMPLES WITH ION-SELECTIVE ELECTRODE

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                    ┌─────────┐
                    │  Start  │
                    └─────────┘
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            ┌──────────────────────────┐
            │       10.1 - 10.2        │
            │        Calibrate         │
            │       Nitrite ISE.       │
            └──────────────────────────┘
                         │
                         ▼
            ┌──────────────────────────┐
            │   11.1 Allow Standards   │
            │      and samples to      │
            │      equilibrate to      │
            │     room temperature.    │
            └──────────────────────────┘
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            ┌──────────────────────────┐
            │   11.2 Rinse electrode   │
            │     with reagent water.  │
            └──────────────────────────┘
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            ┌──────────────────────────┐
            │   11.3 Add 25 mL sample  │
            │   and 25 mL NISS to beaker,│
            │   and measure concentration│
            │     using electrode meter │
            │   and calculate concentration.│
            └──────────────────────────┘
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            ┌──────────────────────────┐
            │   11.4 Drain reference   │
            │     electrode and clean. │
            └──────────────────────────┘
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                    ┌─────────┐
                    │  Stop   │
                    └─────────┘
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